

FLUORINATED HYDROCARBON FLAME SUPPRESSION CHEMISTRY

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ABSTRACT

A comprehensive, detailed chemical kinetic mechanism was developed for fluorinated hydrocarbon destruction and flame suppression. Existing fluorinated hydrocarbon thermochemistry and kinetics were compiled and evaluated. For species where no/incomplete thermochemistry was available, this data was calculated through application of ab initio molecular orbital theory. Group additivity values were determined consistent with experimental and ab initio data. For reactions where no or limited kinetics was available, this data was estimated by analogy to hydrocarbon reactions, by using empirical relationships from other fluorinated hydrocarbon reactions, by ab initio transition state calculations, and by application of RRKM and QRRK methods. The chemistry was modeled considering different transport conditions (plug flow, premixed flame, opposed flow diffusion flame) and using different fuels (methane, ethylene), equivalence ratios, agents (fluoromethanes, fluoroethanes) and agent concentrations. An overview of this work is presented.

INTRODUCTION

During the past year a major effort was conducted at NIST to rate potential replacements (FCs, HFCs, HCFCs) for Halon 1301 (CF₃Br). Halon 1301 has been widely used as a chemical extinguisher in sensitive/critical environments where it is necessary to use fire suppressants that are clean (minimal residue & reactivity), non-toxic, and non-conductive. These environments include aircraft, nuclear reactors, computer rooms, and libraries. Halon 1301 has all of these desirable properties and is extremely effective for fire suppression. Unfortunately, it is also extremely effective for depleting stratospheric ozone (attenuates damaging UV radiation from the sun). Consequently, production and use of Halon 1301 and other high ODP chemicals are being banned on a worldwide level.

The chemical kinetic modeling work presented here is a small part of larger, short term intensive program at NIST evaluating potential replacements for Halon 1301 for the U.S. Air Force, Navy, Army and Federal Aviation Administration. The modeling effort complemented the many experimental measurements in the overall NIST program characterizing the effectiveness of various potential replacements. Our work focused on agent chemistry. However, there are also many physical effects relating to mass and heat transport processes. Many of these issues were addressed by other work in the overall project. This included measurements of PVT properties, discharge dynamics, dispersion mechanics, as well as measurements of extinction effectiveness for more realistic geometries than can be modeled. In our work, we attempted to consider indirectly these physical effects in order to provide a framework for transfer of the results of our simulations to more realistic conditions.

FLUORINATED HYDROCARBON SYSTEM

The major objective of this work was to provide a chemical basis for rationalizing the relative degree of effectiveness of each candidate agent. In order to accomplish this objective, it was necessary to develop a chemical mechanism based on elementary reaction steps for their destruction, their participation in and influence on hydrocarbon flame chemistry, as well as prediction of potential by-products of incomplete combustion. The focus of this work was restricted to chemistry involving only fluoromethanes and fluoroethanes. This included both agents specifically considered in the overall NIST project as replacements (CH₃F₂, CF₃-CH₂F, CF₃-CHF₂, CF₃-CF₃), as well as all other possible fluoromethanes and fluoroethanes. The chlorine-substituted (CHF₂Cl, CF₃-CHF₂Cl) and larger fluorinated hydrocarbon (C₃F₈, C₃F₇H, C₄F₁₀, cyclo-C₄H₈) candidates were not considered in our study because they would significantly increase the complexity of the chemistry. However, the effectiveness of each can be estimated to some degree by analogy to

other agents that were studied using qualitative trends observed and a fundamental understanding of the chemistry.

The complete set of fluoromethanes and fluoroethanes were studied for two basic reasons.

First, when the four considered candidate agents decompose in the flame, they generate a pool of fluorinated hydrocarbon stable species and radicals, which results in the formation of many other fluoromethanes and fluoroethanes. Consequently, in order to adequately describe the decomposition of these four agents (and resultant chemistry), it is necessary to describe the chemistry of all intermediates and products that are created, including most of the other fluoromethanes and fluoroethanes. For example, the lowest energy and primary decomposition pathway for one of the agents, $\text{CF}_3\text{-CF}_3$, involves dissociation of the C-C bond to form (two) CF_3 radicals. The CF_3 radicals then react with methyl radicals (CH_3), which are present in significant concentrations in hydrocarbon flames. This radical-radical combination has two channels whose relative importance depend upon temperature. These channels result in the formation of both a fluoroethylene, $\text{CH}_2=\text{CF}_2$ (and HF), and another fluoroethane, $\text{CH}_3\text{-CF}_3$. In order to correctly predict flame products, the magnitude and rate of heat release in the flame, and ultimately the effectiveness of the added agent, it is also necessary to correctly describe the decomposition of these additional stable fluorinated hydrocarbon species ($\text{CH}_3\text{-CF}_3$, $\text{CH}_2=\text{CF}_2$). When one considers decomposition channels for these molecules, other reaction channels for CF_3 , and relevant chemistry for other candidates, most of the fluoromethanes and fluoroethanes must also be considered.

Second, since there was no directly related experimental work, it was imperative to provide a level of self-consistency by considering a range of modeling parameters, including a variety of reactor/flame geometries, fuels, and (potential) agents. This provided a level of confidence and some validation of the qualitative trends that we observed. Quantitative prediction of the absolute or even relative effectiveness of the specific agents will require benchmarking of the simulations with experimental measurements. It is anticipated that this will be done in the near future.

SPECIES THERMOCHEMISTRY

A large comprehensive reaction set or "mechanism" for fluorinated hydrocarbon chemistry was constructed including C_1 and C_2 stable and radical hydrocarbon species, as well as partially oxidized fluorinated hydrocarbons. Existing thermochemical data was compiled and evaluated. A number of general sources were used [1-5], as were compilations/evaluations [6,7] and individual sources [8-11] for fluorinated hydrocarbons. Where little or no data existed for species of interest (most radicals), we estimated that thermochemistry using either empirical methods (e.g. group additivity) or through applications of ab initio molecular orbital theory. In all cases (experimental, empirical, ab initio), an effort was made to use thermochemistry consistent with data for all species.

Standard hydrogen/oxygen and hydrocarbon thermochemistry was used, most of which can be found in the JANAF tables [2], as can data for F, F_2 , and HF. FO^\bullet , FOO^\bullet , FOF , and HOF species were initially considered, but later excluded, because their concentrations were found to be negligible in the high temperature hydrocarbon flames.

Thermochemical data for the fluoromethanes (CH_3F , CH_2F_2 , CHF_3 , CF_4) can be found in the JANAF tables [2] and has also been reexamined more recently [12]. Thermochemical data for the perfluoromethyl radical ($^\bullet\text{CF}_3$) can be found in the JANAF tables. Reliable, experimentally derived heats of formation for the other fluoromethyl radicals ($^\bullet\text{CH}_2\text{F}$, $^\bullet\text{CHF}_2$) and a more recent value for $^\bullet\text{CF}_3$ can be found in other evaluated sources [9,11,13]. Ab initio calculations of thermochemical data [14-16] for the fluoromethanes and fluoromethyls are consistent with the experimentally derived values. In this work we employed thermochemical data for the fluoromethylenes ($:\text{CHF}$, $:\text{CF}_2$) from the JANAF tables. However, there is some uncertainty (± 10 -20 kJ/mol) in heats of formation for these important species. Furthermore, there have been recent measurements and evaluations [8,10,17,18] and ab initio calculations [14,15] that need to be evaluated. Thermochemical data for $\text{CHF}=\text{O}$, $\text{CF}_2=\text{O}$, $^\bullet\text{CF}=\text{O}$, and $^\bullet\text{CF}$ can be found in the JANAF tables. However, there is some uncertainty (± 10 -20 kJ/mol) in the heats of formation for $\text{CHF}=\text{O}$ and $^\bullet\text{CF}=\text{O}$ as their heats of formation were calculated using average

bond dissociation energies from other compounds. Our ab initio calculations [15] of thermochemistry for these carbonyl fluorides are consistent with the indirect, experimentally derived values. However, given the uncertainty in all of the data, further mechanism refinement will require critical evaluation of these data.

Experimentally derived thermodynamic properties for six fluoroethanes have been compiled and critically evaluated [6]. Data for other fluoroethanes can be found in the DIPPR compilation [5]. There are experimentally derived thermochemical data [8] for only a few fluoroethyl radicals ($\text{CH}_3\text{-CH}_2^\bullet$, $\text{CF}_3\text{-CH}_2^\bullet$, $\text{CF}_3\text{-CF}_2^\bullet$). However, thermochemistry for all fluoroethyl radicals have been calculated using ab initio molecular orbital theory by Tschuikow-Roux et al [19] and for a few fluoroethyl radicals by other workers [14-16]. For consistency, we have used the Tschuikow-Roux et al values. Experimentally derived thermochemistry is available for $\text{CF}_2=\text{CF}_2$ in the JANAF tables [2] and for $\text{CH}_2=\text{CHF}$ and $\text{CH}_2=\text{CF}_2$ in the DIPPR compilation [5]. For the other fluoroethylenes: $\text{CHF}=\text{CHF}(\text{E})$, $\text{CHF}=\text{CHF}(\text{Z})$, $\text{CHF}=\text{CF}_2$, we relied upon ab initio calculations [14]. We are not aware of any experimentally derived thermochemistry for fluorovinyl radicals and, consequently, used our ab initio calculated values [15]. Further mechanism refinement would involve benchmarking ab initio calculations with the experimental data (using bond and group additivity methods) to provide a consistent set of data for the fluoroethanes, -ethyls, -ethylenes, and -vinyls.

REACTION SET DEVELOPMENT

The literature on reaction kinetics for fluorinated hydrocarbons was compiled, reviewed, and evaluated. A large part of our work is based on the pioneering work of Biordi et al [20] and Westbrook [21]. Due to the limited nature of this paper, the reaction set that we developed can only be outlined here. Many of the rate constants can be found in the NIST Chemical Kinetics Database [22].

Utilizing species identified as potentially important, we constructed a grid of possible reactions. Existing chemical rate data involving these fluorinated species were then compiled and evaluated. Where rate data was available over a limited temperature range or at different pressures (for unimolecular or chemically activated steps), RRKM and QRRK methods were used to estimate the rate constant temperature (and pressure) dependence and to predict relative rates where multiple product channels were possible. Where no rate data were available for potential reactions, the rate constants were estimated by analogy to hydrocarbons or substituted hydrocarbons. The rate constant prefactors were adjusted for reaction path degeneracy and activation energies were adjusted empirically based on relative heats of reaction or bond energies.

Initially, upper limits were used for estimated rate constants. If as a result of simulation under a variety of conditions, it was observed that a specific reaction contributed to the chemistry and its rate constant was an upper limit estimate, then its value was reexamined and possibly refined. For important contributing reactions, where no good analogy was available, where significant uncertainty existed in the barrier (generally reactions with tight transition states and modest-to-large barriers), or where energetically similar product channels were possible, ab initio methods were used to calculate the geometries and energies of the transition states. RRKM methods were then applied to obtain the temperature (and pressure) dependence of the rate constant.

CONTRIBUTING REACTIONS

The hydrocarbon and hydrogen/oxygen reaction subsets of the mechanism were derived from the Miller/Bowman mechanism [23]. This reaction subset consists of about 30 species and 140 reactions. A number of species important in fuel rich flames (e.g. C_2H) were eliminated from the mechanism. A number of species important in fuel lean flames (e.g. CH_3OH) were added using kinetics from other validated mechanisms [20]. Rate constants for a few reactions (e.g. CH_3+OH) were also adjusted to provide correct fall-off and product channel ratios. The hydrogen/oxygen/fluorine reaction subset consists of only 3 species and about 8 reactions, although many more were initially considered. Three reactions were determined to be most important: combination of H and F atoms to form HF and H atom abstractions from H_2 and H_2O by F radicals.

The C₁ reaction subset consists of about 15 species and 200 reactions. Both thermally- and chemically-activated fluoromethane decompositions are included (e.g. $\text{CH}_2\text{F}_2 \Rightarrow \text{:CHF} + \text{HF}$ and $\bullet\text{CHF}_2 + \text{H}$

\Rightarrow :CHF + HF). Fluoromethane decompositions via abstraction of H atoms by H, O, and OH radicals were also considered with abstractions by OH and H the major decomposition pathways. The fluoromethyls produced here were destroyed by several pathways whose relative importance were sensitive to conditions: reactions with H radicals, CH₃ radicals, and oxygen-containing species (O₂, O, OH). The products of the latter reactions consist of carbonyl fluorides (i.e. CF₂O, CHF=O, *CF=O) and HF or other elimination products (e.g. *CHF₂ + OH \Rightarrow CHF=O + HF). It was seen almost exclusively that any reaction channel with an HF product was the dominant channel. The fluoromethyls (:CHF, :CF₂) were largely created by combination of fluoromethyls and H radicals via chemically-activated fluoromethanes (and HF elimination). The fluoromethyls were predominantly destroyed similarly by combination with H radicals via chemically-activated fluoromethyls (and HF elimination creating *CH and *CF). *CF radicals created here were largely consumed by reactions with H₂O and O₂ resulting in CHF=O and *CF=O formation.

Typical reaction pathways for the decomposition of two potential agents, CH₂F₂ and CHF₃, are shown in Figure 1.

The C₂ reaction subset consisted of about 40 species and 400 reactions. Due to the limited nature of this paper, this reaction set cannot be described here in detail. Briefly, the fluoroethane destruction pathways (like fluoromethanes) consist of thermally- and chemically-activated decompositions and H atom abstraction reactions. Fluoroethyl radicals can react with H radicals (like fluoromethyls) creating fluoroethylenes (via chemically activated fluoroethanes and HF elimination). Fluoroethyl radicals can also react with oxygen-containing species (O₂, O, OH) resulting in the formation of oxidized fragments (e.g. CF₃-CF₂* + O \Rightarrow *CF₃ + CF₂=O). Fluoroethylenes (produced from thermally- and chemically-activated fluoroethane decompositions) are predominantly destroyed via reaction with O radicals resulting in the formation of oxidized fragments (e.g. CH₂=CF₂ + O \Rightarrow *CH=O + *CHF₂). Fluoroethylenes are also destroyed to a lesser degree through H atom abstraction by radicals such as OH, resulting in formation of fluorovinyl radicals (e.g. CH₂=CF₂ + OH \Rightarrow CF₂=CH* + H₂O). Fluorovinyl radicals (like fluoromethyl and fluoroethyl radicals) are destroyed via reactions with H radicals, as well as with oxygen-containing species. However, it was observed that the fluorovinyl radicals established a dynamic equilibrium with the parent fluoroethylenes, irrespective of the specific creation and destruction pathways.

PREMIXED FLAME CALCULATIONS

Adiabatic, freely-propagating, premixed flame calculations [25] were performed utilizing the reaction mechanism briefly outlined above. Typically, fuel lean CH₄/air conditions were modeled in order to be most sensitive to flame speed changes and (in a practical sense) since agents are added to the air supply. More realistic would be to simulate agent effects in a diffusion flame. We have performed a few opposed flow diffusion flame calculations; however, those results are preliminary and ongoing.

A summary of the effects on adiabatic flame temperature and speed are shown in Figure 2 for addition of a variety of "agents" to a CH₄/air flame (equivalence ratio of 0.65). In addition to potential fluorinated hydrocarbon agents: CF₄, CHF₃, CH₂F₂, CF₃-CF₃, CF₃-CF₂H, and CF₃-CFH₂, other species were added to investigate the effect of heat capacity and heat release on flame speed changes. These reference "agents" include N₂, H₂O, CO₂, HF, and CH₄. In order to correct for differences in heat capacities for the different "agents", the amount of added "agent" was normalized to an equivalent amount of N₂, adjusting for relative heat capacities at 1500K. For example, addition of 1% CF₄ (with C_p=105 J/mol/K) would be roughly equivalent to addition of 3% N₂ (with C_p=35 J/mol/K). Using heat capacities at other temperatures (1000-2000K) had little impact on the relative normalized mole fractions.

In Figure 2a, it can be seen that the effect of the various agents on flame temperature can be bracketed by addition of inert molecules (N₂, H₂O, CO₂, HF), where there is decrease in flame temperature, and by addition of more fuel (CH₄), where there is an increase in flame temperature. The decrease in flame temperature upon addition of the inerts is due to dilution and increased heat capacity of the mixture. The increase in flame temperature upon addition of more fuel is due to increased heat release as the mixture becomes more rich. Addition of agents which are more fuel-

like results in a larger increase in flame temperature. All of the fluorinated hydrocarbons are fuels since they all eventually decompose, burn, and form CO_2 , H_2O , and HF (liberating heat). At one extreme is CF_4 , very little of which decomposes in the flame, and consequently, there is only a small increase in flame temperature relative to addition of inerts. On the other extreme is CH_2F_2 , which completely burns forming highly exothermic products CO_2 and HF . In Figure 2b, a range of effects on flame speed for the various added agents can be observed. For the inert molecules and the nearly inert fluorinated hydrocarbons (CF_4 , $\text{CF}_3\text{-CF}_3$), a decrease in flame speed is observed consistent with dilution of the mixture. On the other extreme, for CH_4 (the fuel) and CH_2F_2 (a slightly poorer fuel), an increase in flame speed is observed.

Of the various agents considered, only CHF_3 was seen to have any chemical effect in flame suppression. Figure 2 shows that although there is an increase in flame temperature upon CHF_3 addition, there is also a decrease in flame speed relative to inert molecule addition. Inspection of reaction pathways for CHF_3 and other agents (see Figure 1) reveals that a significant amount of decomposed CHF_3 results in the formation of the relatively unreactive perfluorocompound carbonyl fluoride ($\text{CF}_2=\text{O}$). Decomposition of $\text{CF}_2=\text{O}$ occurs only very slowly via reaction with either H radicals (H addition + HF elimination) or with H_2O (through a hot fluoroformic intermediate). For all other agents, this $\text{CF}_2=\text{O}$ bottleneck is avoided.

SUMMARY

These simulations are consistent with qualitative trends observed in experimental measurements of agent effectiveness in the work by others in other parts of the overall project at NIST. In order to quantitatively predict agent effectiveness, experimental validation of the mechanism will be necessary and is currently underway.

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FIGURE 1. Typical Reaction Pathways for CH_2F_2 and CHF_3

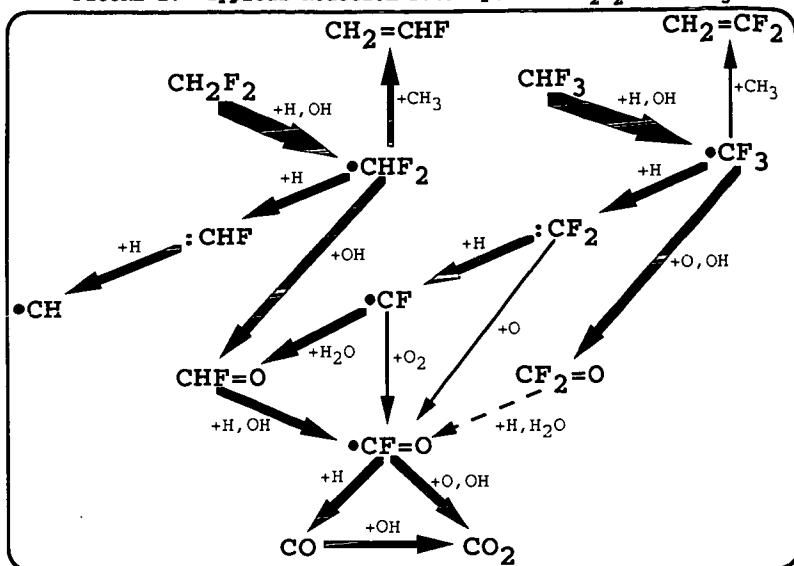


FIGURE 2. Effect of Agents on Flame Temperature and Speed

